THE INFLUENCE OF STERIC HINDRANCE ON THE OXIDATIVE CLEAVAGE OF PROPYLENE GLYCOLS

BY

TZI-LIEH TAN

B. S., University of Chungking, 1940
M. S., University of Illinois, 1946

AN ABSTRACT OF A THESIS

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Introduction

Treatment with periodic acid or lead tetraacetate constitutes a general method of cleaving glycols to carbonyl-containing products (1). Since this type of reaction usually proceeds to completion at room temperature, it has been widely used for analytical as well as synthetic purposes.

In connection with the synthesis of diarylacetaldehydes corresponding to the stable 2,2-diarylvinyl alcohols (2), it was decided to study the action of periodic acid and lead tetraacetate on the propylene glycols which are structurally related to the diarylacetaldehydes.

Discussion of Results

3-Mesityl - 3 - phenyl-1,2-propanediol and 3 - isoduryl - 3-phenyl-1,2-propanediol were prepared by the hydrogenation of mesitylphenyl- and isodurylphenylpyruvaldehyde, respectively. The pyruvaldehydes were made from the corresponding 1,1-diaryl-2-propanones by oxidation with selenium dioxide.

1,3-Dimesityl-3-phenyl-1,2-propanediol and 1,3-dimesityl-3-*p*-tolyl-1,2-propanediol were prepared from mesitalacetomesitylene (3). Condensation of this chalcone with phenyl- and *p*-tolylmagnesium bromides and subsequent treatment of the resulting enols with oxygen gave 1,3-dimesityl-3-phenyl-1-propen-1-ol and 1,3-dimesityl-3-*p*-tolyl-1-propen-1-ol peroxides. The enol peroxides were reduced to hydroxy ketones with potassium iodide and acetic acid. High pressure hydrogenation of the hydroxy ketones in the presence of a copper chromite catalyst yielded the propylene glycols.

Attempts were made to synthesize 1,3,3-trimesityl-1,2-propanediol and 1-mesityl-3-isoduryl-3-phenyl-1,2-propanediol in a similar manner. The enol peroxides were obtained by condensation of mesitalacetomesitylene and isoduralacetomesitylene with mesityl- and phenylmagnesium bromide, respectively. They were reduced smoothly to the hydroxy ketones with potassium iodide and acetic acid. Treatment of the hydroxy ketones with hydrogen, however, caused isomerization. The isomers resisted hydrogenation.

Oxidation of the glycols by lead tetraacetate gave the corresponding acetoxydiarylacetaldehydes (4). The results were explained by the assumption of attack of the diarylacetaldehydes, formed in the oxidation, by the reagent.

When 3-mesityl-3-phenyl-1,2-propanediol and 1,3-dimesityl-3-phenyl-1,2-propanediol were oxidized with periodic acid, mesitylphenylacetaldehyde was isolated. It is the first example of a diarylacetaldehyde corresponding to a stable 2,2-diarylvinyl alcohol. The aldehyde was converted to 2-mesityl-2-phenylvinyl alcohol by heating at 150° for two hours or by treatment with ethanolic potassium hydroxide. The structure of the aldehyde was confirmed by infrared spectrum measurements and by condensation with phenylmagnesium bromide.

Oxidation of 1,3-dimesityl-3-*p*-tolyl-1,2-propanediol with periodic acid yielded mesityl-*p*-tolylacetic acid as one of the products. The isolation of the acid indicated the formation of mesityl-*p*-tolylacetaldehyde as an initial product in the oxidation.

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VITA

The author was born in Tienkiang, Szechuan, China, on January 4, 1918. He attended the elementary schools in that town and a professional school in Chungking. In 1936, he enrolled in the University of Chungking from which he was graduated with the degree of Bachelor of Science in 1940. After a period spent as a teaching assistant at his Alma Mater and as a laboratory assistant in the Institute of Medical Administration, Ministry of War, China, he came to the United States. He entered the University of Illinois in the spring of 1945 and received the degree of Master of Science in 1946. From October, 1946, to September, 1947, he held a University Fellowship.

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